

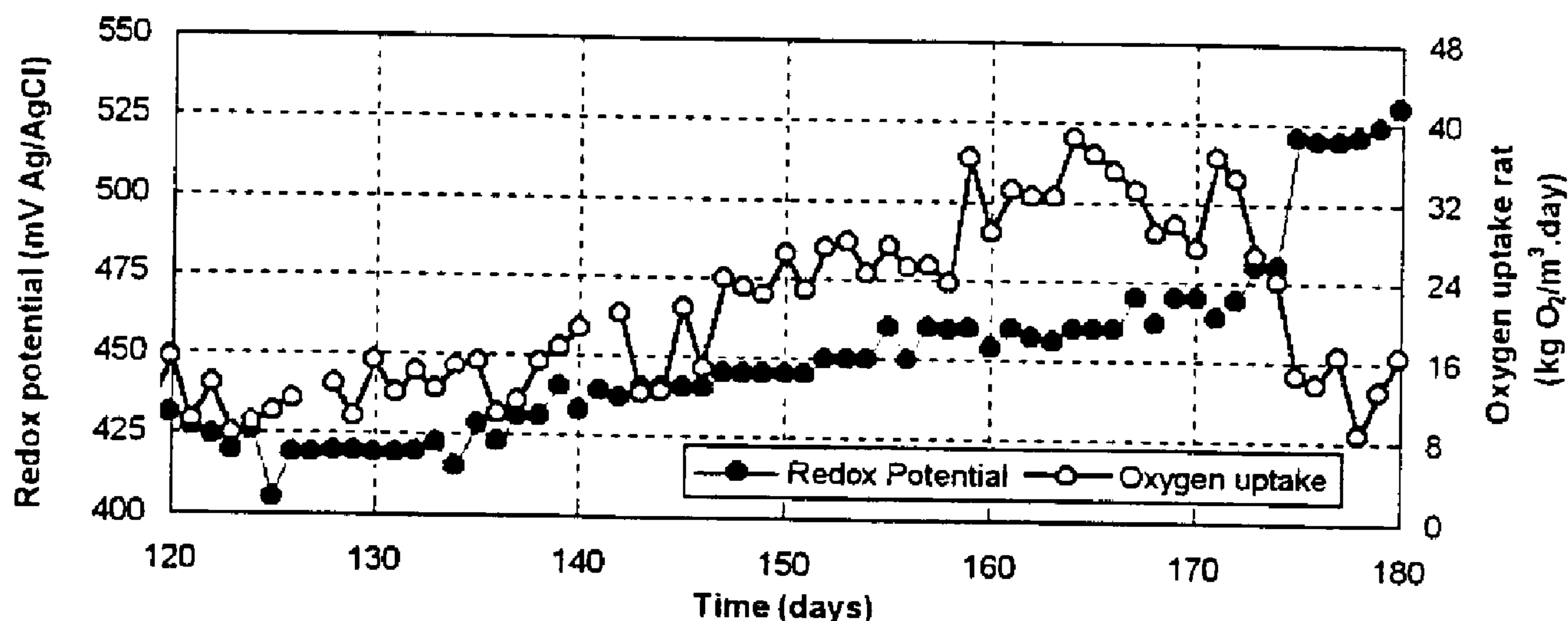


(86) Date de dépôt PCT/PCT Filing Date: 2000/10/23
(87) Date publication PCT/PCT Publication Date: 2001/05/03
(45) Date de délivrance/Issue Date: 2009/09/01
(85) Entrée phase nationale/National Entry: 2002/04/24
(86) N° demande PCT/PCT Application No.: ZA 2000/000196
(87) N° publication PCT/PCT Publication No.: 2001/031072
(30) Priorités/Priorities: 1999/10/28 (ZA99/6790);
1999/11/11 (ZA99/7057)

(51) Cl.Int./Int.Cl. *C22B 3/18* (2006.01),
C22B 15/00 (2006.01)
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(54) Titre : TECHNIQUE PERMETTANT DE PROCEDER A UNE LIXIVIATION BIOLOGIQUE AVEC MAITRISE DU
POTENTIEL D'OXYDO-REDUCTION

(54) Title: A METHOD OF OPERATING A BIOLEACH PROCESS WITH CONTROL OF REDOX POTENTIAL



(57) Abrégé/Abstract:

A method of operating a bioleach process for the leaching of a sulfide bearing ore or concentrate includes subjecting a bioleach slurry which includes dissolved oxygen, dissolved carbon dioxide, sulphide and microorganisms to a bioleach stage, and controlling the redox potential of the bioleach slurry within a predetermined range.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 May 2001 (03.05.2001)

PCT

(10) International Publication Number
WO 01/31072 A1

(51) International Patent Classification⁷: C22B 3/18, 15/00

(21) International Application Number: PCT/ZA00/00196

(22) International Filing Date: 23 October 2000 (23.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

99/6790	28 October 1999 (28.10.1999)	ZA
99/7057	11 November 1999 (11.11.1999)	ZA

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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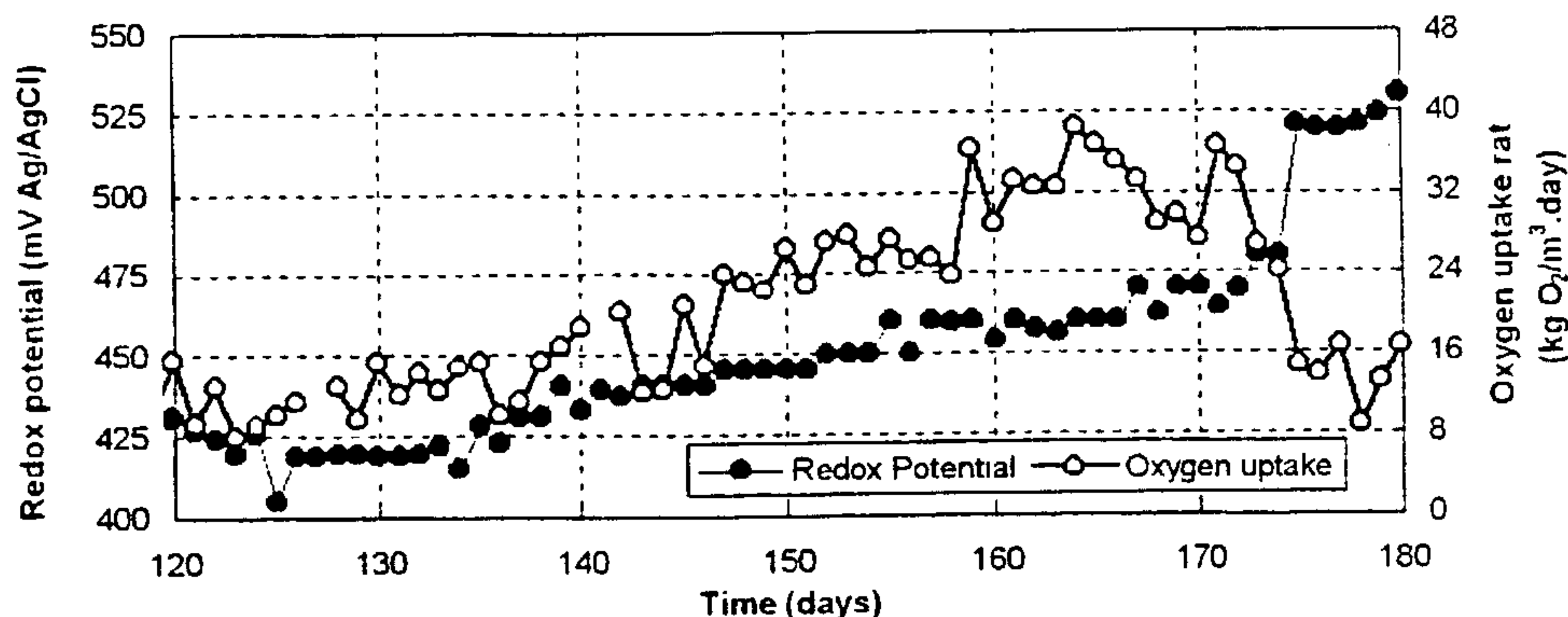
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Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A METHOD OF OPERATING A BIOLEACH PROCESS WITH CONTROL OF REDOX POTENTIAL



(57) Abstract: A method of operating a bioleach process for the leaching of a sulfide bearing ore concentrate includes subjecting a bioleach slurry which includes dissolved oxygen, dissolved carbon dioxide, sulphide and microorganisms to a bioleach stage, and controlling the redox potential of the bioleach slurry within a predetermined range.

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A METHOD OF OPERATING A BIOLEACH PROCESS WITH CONTROL OF REDOX POTENTIAL

THIS INVENTION relates to a method of operating a bioleach process. In particular, it relates to a method of operating a bioleach process for the leaching of a sulfide bearing ore or concentrate slurry.

5 It is now becoming generally accepted that a primary mechanism for leaching of sulphide minerals in bioleaching processes is (chemical) ferric oxidation, where the bacteria act as the catalyst to promote ferrous-to-ferric iron oxidation by oxygen. The leaching of sulphide minerals in acidic sulphate liquors or slurries is strongly influenced by the redox potential of the liquor or slurry. In
10 bioleach processes, the redox potential of the leach slurry or solution is determined largely by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ concentration ratio. A sulphide mineral such as pyrite (FeS_2) has a high rest potential and oxidation is consequently extremely slow at redox potentials below 450 mV (vs. Ag/AgCl reference electrode) but increases rapidly as the redox potential is increased to around 650
15 mV. This can be compared to the copper sulphide mineral, chalcocite (Cu_2S) that has a low rest potential and will leach rapidly even at a low redox potential around 400 mV. The leaching of chalcopyrite (Cu Fe S_2) is more complex. Leaching of this mineral is enhanced at low redox potentials (380-480 mV), but is inhibited at high redox potentials due to passivation of the mineral surface.

20 Bioleaching processes employ mixed cultures of microorganisms or bacteria. These microorganisms may include low temperature (mesophilic) types which prefer temperatures in the range 30-45 °C, moderately thermophilic types

which prefer temperatures in the range 45-60 °C and extreme thermophilic types which prefer temperatures in the range 60-90 °C. Low temperature bacterial cultures, for example, are composed of *Thiobacillus ferro-oxidans*, *Thiobacillus thio-oxidans* and *Leptospirillum ferro-oxidans*. These individual bacteria also exhibit optimum activity at different redox potentials. Thus, *Leptospirillum* exhibits optimum activity at redox potentials of 600-650 mV, while *Thiobacillus ferro-oxidans* exhibits optimum activity at redox potentials around 450-500 mV.

In a continuously operated bioleach process treating finely milled sulphide concentrate in agitated tanks, the conditions are usually set so that optimum conditions are provided for bacterial activity. Under these conditions, the bacterial cell growth rate and oxidative activities will be at a maximum and the rate of sulphide leaching observed represents a condition where the rate of bacterial ferric iron production and the rate of ferric iron consumption for sulphide oxidation are balanced. For bioleaching processes treating a pyrite feed, it is usually found that a relatively high redox potential is observed and that the bacteria predominating in the process are *Leptospirillum ferro-oxidans*. For a pyrite bioleach process this could therefore be regarded as the normal or "natural" operating condition for the process. Indeed, a commercial process would be engineered to ensure that these conditions are provided. For minerals with lower rest potentials, such as chalcocite, oxidation by ferric will occur at lower redox potentials. For chalcocite, it has been speculated that the normal operating condition will be a relatively low redox potential and that under these conditions *Thiobacillus ferro-oxidans* may be the predominating bacterium (this is often observed in practice).

All bioleaching bacteria live and grow using solely inorganic nutrients. The bacteria use the oxidation of ferrous iron and sulphur (or sulphide) by oxygen as the energy sources that allow them to grow and survive. In addition to oxygen, other essential nutrients required by the bacteria are carbon dioxide, nitrogen and phosphorus. When all of these individual nutrients are present (in

solution) in excess the bacteria are capable of growing at a maximum rate and exhibiting the maximum rates of oxidation of ferrous iron and sulphur.

In the engineering design of bioleach processes, a key consideration is to ensure that the supplies of oxygen and carbon dioxide are sufficient, and the usual design criterion is to ensure that they will always be present in excess. The primary supplies of these bacterial nutrients are from air supplied to the process. In the case of tank leaching of sulphide concentrates the air is sparged into the tank and has to be transferred or dissolved into solution, so that it becomes available to the bacteria, by the process of mass transfer. The demand for oxygen by the process is high – for example, the oxidation of one kilogram of pyrite requires the supply of one kilogram of oxygen. However, oxygen and carbon dioxide are only sparingly soluble in water at ambient temperature and atmospheric pressure and hence the mass transfer supply of these nutrients becomes a key process engineering design and cost consideration.

The applicants are aware of US 5,397,380 relating to a process for the treatment of complex metal sulphide materials and for the recovery of metal values from such materials. The process involves first subjecting the material to a leaching process under conditions such that sulphide-sulphur is oxidised to sulphate and such that oxidised iron and impurities such as As will pass into solution, whereafter the leaching residue is melted for conventional pyrometallurgical recovery of the metal values. The applicants are also aware of JP-A-10265864 for a method of leaching sulphur-containing copper using bacteria under conditions of a high redox potential in the range of 550-750 mV. A relatively strong acid concentration is used at a set redox potential of 550-750 mV to increase the rate of leaching. The applicants are also aware of an article by P d'HUGUES et al entitled "Bioleaching of a cobaltiferous pyrite: a continuous laboratory-scale study at high solids concentration" published in Minerals Engineering, Vol. 10, No.5, pp. 507-527 in 1997. This reference deals with the

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bioleaching of a cobaltiferous pyrite carried out at 20 % solids in a continuous laboratory-scale unit composed of four stirred reactors arranged in cascade, and investigates the optimisation of the bioleach process using mechanically agitated and aerated reactors. Lastly, the applicants are aware of US 5,007,620, dealing with the mechanical design and operation of a bioleaching reactor used for slurry bioleaching processes that provide, in particular, for the provision of a specific low-power consumption mechanism for aeration of the slurry and for slurry suspension. This involves the injection of air as a source of oxygen into the reactor through porous membranes diffusers specifically arranged and operated in the base of the reactor.

According to the invention, there is provided a method of operating a bioleach process for the leaching of a sulfide bearing ore or concentrate, the method including

subjecting a bioleach slurry which includes dissolved oxygen, dissolved carbon dioxide, sulphide and microorganisms to a bioleach stage; and controlling the redox potential of the bioleach slurry within a predetermined range.

The method may include ensuring that both the dissolved oxygen concentration and the dissolved carbon dioxide concentration in the bioleach slurry remains above respective lower concentration limits, the respective lower concentration limits being selected to ensure that the growth of the microorganisms is not limited by a too low concentration of either the dissolved oxygen or the dissolved carbon dioxide in the bioleach slurry.

The redox potential of the bioleach slurry may be controlled within the predetermined range by controlling the concentration of at least one of the dissolved oxygen and the dissolved carbon dioxide in the bioleach slurry.

5 In a preferred embodiment of the invention, the redox potential of the bioleach slurry is controlled within the predetermined range by controlling the concentration of the dissolved carbon dioxide in the bioleach slurry.

10 Typically, at least some of the carbon dioxide and the oxygen is supplied to the bioleach slurry as air. The method may also include supplying carbon dioxide and oxygen to the bioleach slurry in the form of carbon dioxide-enriched air. Instead, the carbon dioxide may be supplied as a separate gas stream. In another embodiment, the bioleach slurry may be acidic and the method may include supplying carbon dioxide to the bioleach slurry in the form of limestone. In a further embodiment, the bioleach slurry may include microorganism with enzymes in their cells which are capable of reacting with urea to release carbon dioxide, the method then including supplying carbon dioxide to the bioleach slurry in the form of urea.

15 When the redox potential is controlled by controlling the concentration of the dissolved oxygen in the bioleach slurry, the dissolved oxygen concentration may be controlled by controlling the rate of air supply to the bioleach slurry, or by controlling the rate of supply of a separate oxygen gas stream.

20 In one embodiment of the invention, the dissolved carbon dioxide or dissolved oxygen concentration in the bioleach slurry is controlled by maintaining a constant feed rate of carbon dioxide or oxygen to the bioleach slurry, and manipulating the mean pulp residence time in the bioleach stage. The rate of growth of the microorganisms, and therefore the rate of sulphide oxidation,

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changes with residence time, generally increasing as the residence time is decreased.

In another embodiment of the invention, the dissolved carbon dioxide or dissolved oxygen concentration in the bioleach slurry is controlled by maintaining a constant feed rate of carbon dioxide or oxygen to the bioleach slurry, and a constant mean pulp residence time in the bioleach stage, and adding ore or concentrate, in a dry solids form, to the bioleach slurry. The supply of additional sulphide solids acts to create an increased demand for oxygen and carbon dioxide, thereby providing a means of controlling the concentration of carbon dioxide or oxygen in the bioleach slurry.

The bioleach slurry may be agitated. Thus, in a further embodiment of the invention, the dissolved carbon dioxide or dissolved oxygen concentration in the bioleach slurry is controlled by maintaining a constant feed rate of carbon dioxide or oxygen to the bioleach slurry, and by manipulating the agitation of the bioleach slurry, thereby controlling the rate of dissolution of carbon dioxide or oxygen in the slurry. For a given impeller type, the gas-liquid mass transfer coefficient for carbon dioxide or oxygen is primarily dependent on stirrer speed.

The ore or ore concentrate may include pyrite as an undesirable component, in which case the redox potential may be controlled in the range of 380 mV to 450 mV relative to a Ag/AgCl reference electrode, thereby inhibiting leaching of the pyrite while selectively leaching desirable sulphide minerals present in the ore or ore concentrate with a rest potential which is lower than the rest potential of pyrite.

The ore or ore concentrate may include chalcopyrite as a predominant sulphide component, in which case the redox potential may be controlled in the range of 380 mV to 480 mV relative to a Ag/AgCl reference electrode thereby to promote the rate and extent of chalcopyrite oxidation.

The microorganisms may be selected from mesophiles such as *Thiobacillus ferro-oxidans*, *Thiobacillus thio-oxidans*, *Thiobacillus caldus* and *Leptospirillum ferro-oxidans*, moderate thermophiles such as *Sulfobacillus* and *Acidimicrobium* species, extreme thermophiles such as *Sulfolobus* and *Acidianus* species, and mixtures thereof.

The lower limit of the concentration of the dissolved carbon dioxide in the bioleach slurry may be at least 0,15 ppm. Typically, the concentration of the dissolved carbon dioxide in the bioleach slurry is maintained at or above at least 0,2 ppm for a moderately thermophilic bacterial culture. The lower limit of the concentration of the dissolved oxygen in the bioleach slurry may be at least 0,2 ppm for a moderately thermophilic bacterial culture. The lower limit of the concentration of the dissolved carbon dioxide in the bioleach slurry may be at least 0,6 ppm, typically at least 0,7 ppm, for an extremely thermophilic bacterial culture. The lower limit of the dissolved oxygen in the bioleach slurry may be at least 0,5 ppm, typically at least 0,7 ppm, for an extremely thermophilic bacterial culture. It is however to be appreciated that the lower limits for the concentration of the dissolved oxygen and the dissolved carbon dioxide are dependent on factors such as the microorganisms used and the conditions of the bioleach slurry (pH, temperature), and that the appropriate lower limits can be established for each bioleach process by means of routine experimentation.

The invention will now be described by way of the following non-limiting Examples and the accompanying drawings.

In the drawings

Figure 1 shows a graph of carbon dioxide consumption (r_{CO_2}) against bulk concentration of dissolved carbon dioxide (C_{CO_2}) in a bioleach slurry of a first sulphide minerals concentrate, resulting from test work as set out in Example 1 below;

Figure 2 shows a graph of carbon dioxide consumption (r_{CO_2}) against bulk concentration of dissolved carbon dioxide (C_{CO_2}) in a bioleach slurry of a second sulphide minerals concentrate, resulting from test work as set out in Example 1 below;

5 Figure 3 shows a graph of oxygen consumption (r_{O_2}) against bulk concentration of dissolved oxygen (C_{O_2}) in the bioleach slurry of the second sulphide minerals concentrate, resulting from test work as set out in Example 1 below;

10 Figure 4a shows a graph of redox potential and air flow against time resulting from test work as set out in Example 2 below;

 Figure 4b shows a graph of redox potential and bulk concentration of dissolved carbon dioxide against time resulting from test work as set out in Example 2 below;

15 Figure 4c shows a graph of redox potential and bulk concentration of dissolved oxygen against time resulting from test work as set out in Example 2 below;

 Figure 4d shows a graph of redox potential and oxygen uptake against time resulting from test work as set out in Example 2 below;

20 Figure 4e shows a graph of redox potential and copper concentration against time resulting from test work as set out in Example 2 below;

 Figure 5a shows a graph of redox potential and oxygen uptake against time resulting from test work as set out in Example 2 below;

25 Figure 5b shows a graph of bulk dissolved oxygen concentration and bulk dissolved carbon dioxide concentration against time resulting from test work as set out in Example 3 below;

 Figure 5c shows a graph of leached copper concentration and leached iron concentration against time resulting from test work as set out in Example 3 below;

30 Figure 6 shows a graph of oxygen consumption (r_{O_2}) against bulk concentration of dissolved oxygen (C_{O_2}) in a bioleach slurry of the second

sulphide minerals concentrate, resulting from test work as set out in Example 4 below; and

Figure 7 shows a graph of carbon dioxide consumption (r_{CO_2}) against bulk concentration of dissolved carbon dioxide (C_{CO_2}) in a bioleach slurry of the second sulphide minerals concentrate, resulting from test work as set out in Example 4 below.

A series of tests were carried out in small-scale continuously operated pilot plant facilities treating copper sulphide concentrates. For the purposes of the tests described in the Examples the plant was operated as a single-stage 2 or 25 litre volume reactor. Normally these facilities would be operated as a number of reactors operated in series. The 25 litre reactors are of a conventional design with a variable speed agitator providing mixing of the pulp in the reactor via a standard 6-blade flat-blade Rushton turbine at the bottom of a stirrer shaft in combination with a 6-blade 45° axial flow impeller situated above. The 2 litre reactor is similar, but with a single 6-blade flat-blade Rushton turbine at the bottom of the stirrer shaft. Aeration was via a sparge pipe situated below the Rushton turbine. The tank was fully baffled. Control of the operating temperature in the reactor was achieved using a temperature controller via a temperature probe and immersion heater in the reactor. For continuous operation, a slurry of fine milled concentrate was fed to the reactor from a feed make-up tank via a peristaltic pump. Pulp overflow from the 25 litre reactor was via a gravity overflow to a collection tank. For the 2 litre reactor, the pulp overflow was pumped from the reactor at the same flow rate as the feed slurry via a peristaltic pump. The air supplied to the tank was supplemented, if necessary, with additional carbon dioxide gas. Inlet gas to the reactor and exit gas above the pulp in the reactor were analysed for oxygen and carbon dioxide contents using gas analysers. This allowed the rate at which these gases were consumed in the reactor to be calculated from simple mass balances. The dissolved oxygen content in the pulp was measured using a dissolved oxygen probe. The redox

potential and pH of the pulp was determined using probes immersed in the pulp. Copper (and iron) concentrations were obtained by analysis of liquor samples removed from the reactor.

EXAMPLE 1

5 In this Example a first set of tests was carried out to determine the effect of dissolved oxygen and carbon dioxide levels on the rates of sulphide oxidation and bacterial growth for a moderately thermophilic bacterial culture at 45 °C. Two concentrates were used in these tests. The first concentrate was a polymetallic sulphide concentrate containing (by mass) 42% chalcopryite, 24.5%
10 sphalerite (ZnS), 16% galena (PbS), 4% pyrite, 2% bornite (Cu_5FeS_4), 2% covellite (CuS), the remaining mass comprising predominantly gangue minerals. The second concentrate (concentrate 2) was a predominantly chalcopryite concentrate containing (by mass) 60% chalcopryite (CuFeS_2) and 20% pyrite (FeS_2), the remaining mass comprising predominantly gangue minerals.

15 The 25 litre reactor was used in this series of tests. The concentrates fed to the reactor had been milled to give $d_{90} = 10\text{-}12 \mu\text{m}$. The concentrate slurry fed to the bioleach reactor from the feed make-up tank contained 10 % (mass basis) of concentrate in an inorganic nutrient solution. This nutrient solution contained $(\text{NH}_4)_2\text{SO}_4$, 3 g/l, K_2HPO_4 , 0.5 g/l, MgSO_4 , 0.2 g/l
20 and $\text{Ca}(\text{NO}_3)_2$, 0.05 g/l.

 Initially, the bioleach reactor was operated under conditions where it was estimated that both oxygen and carbon dioxide would be present at excess concentrations, in other words, that the sulphide oxidation and bacterial growth rates would not be limited by the concentrations of these components. The
25 supply of oxygen and carbon dioxide from the air supply to the reactors into the leach solution occurs by the process of gas-liquid mass transfer. Under steady operating conditions, the rates of oxygen and carbon dioxide gas-liquid mass

transfer will be equal to the rates at which these components are consumed by the bacteria to drive the oxidation and growth reactions occurring in the reactor.

The rates of gas-liquid mass transfer for oxygen follow the equation:

$$r_{O_2} = K_{LO_2}(C^*_{O_2} - C_{O_2}) \quad \dots\dots\dots (1)$$

where r_{O_2} = the rate of oxygen transferred and consumed ($\text{kgO}_2/\text{m}^3\cdot\text{day}$), K_{LO_2} = overall gas-liquid mass transfer coefficient for oxygen, $C^*_{O_2}$ = concentration of oxygen that would be in equilibrium with the partial pressure of oxygen in the gas phase in the reactor (kg/m^3) and C_{O_2} = bulk concentration of oxygen measured in the slurry in the reactor (kg/m^3). The mass transfer coefficient, K_{LO_2} , will depend primarily on the type, size and design of impeller system employed, the impeller stirring speed and the air flow rate. The $(C^*_{O_2} - C_{O_2})$ term in equation (1) represents a concentration difference driving force, where the magnitude of this driving force can be increased by increasing the partial pressure of oxygen in the gas supplied to the reactor, since this will, in turn, increase the value of $C^*_{O_2}$.

A similar equation can be written for carbon dioxide consumption:

$$r_{CO_2} = K_{LCO_2}(C^*_{CO_2} - C_{CO_2}) \quad \dots\dots\dots (2)$$

In the case of carbon dioxide the difficulty arises that, unlike dissolved oxygen, the dissolved carbon dioxide in the slurry, C_{CO_2} , cannot be measured directly.

It has been shown, however, that:

$$K_{LCO_2} = 0.89 K_{LO_2} \quad \dots\dots\dots (3)$$

Equations (1), (2) and (3) can thus be combined to give:

$$C_{CO_2} = C^*_{CO_2} - [1.124(r_{CO_2}/r_{O_2})(C^*_{O_2} - C_{O_2})] \quad \dots\dots\dots (4)$$

Since r_{CO_2} and r_{O_2} are estimated from the carbon dioxide and oxygen mass balances, the values of $C^*_{CO_2}$ and $C^*_{O_2}$ are estimated from exit gas analyses, and C_{O_2} is measured, equation (4) allows an estimate of C_{CO_2} to be made. This was the method used for estimating C_{CO_2} in all the test results described.

Once steady operation had been achieved in these tests, the mass transfer supply of oxygen was changed by varying the airflow rate while keeping all other operating conditions constant. The mass transfer supply of carbon dioxide to the reactor was changed through changes in both the airflow rate and in the inlet air carbon dioxide content. The reactor was allowed to reach steady operating condition once more and the rates of oxygen and carbon dioxide were then measured from mass balances in oxygen and carbon dioxide across the reactor. The results of these tests are shown in Figures 1 and 2 in terms of r_{CO_2} vs. C_{CO_2} (concentrates 1 and 2, respectively) and in Figure 3 in terms of r_{O_2} vs. C_{O_2} (concentrate 2). It is clear from Figures 1 and 2 that for both concentrates r_{CO_2} is unaffected by decreases in C_{CO_2} until the concentration falls to a value of between 0.15 and 0.2 ppm. Below this critical value there is an approximately linear decrease in r_{CO_2} .

A similar type of trend is seen for oxygen in Figure 3. In this case, r_{O_2} was unaffected by decreases in C_{O_2} down to approximately 0.2 ppm. This approaches the lowest concentration that can be distinguished accurately using the dissolved oxygen probe being used. It can be concluded from this result that the critical value of C_{O_2} is < 0.2 ppm for the bacterial culture used and the conditions employed in the test. It was noted however that at the dissolved oxygen concentration below the critical level the process was relatively unstable. Hence, the preferred method of control is that based on the control of the carbon dioxide supply, where the process exhibits a higher level of stability.

The critical values for C_{CO_2} and C_{O_2} identified above should be regarded as characteristic of the moderately thermophilic bacterial culture for bioleaching of the copper concentrates used and the specific leach conditions used. These critical concentrations can be identified for different bacterial cultures and the specific bioleaching process conditions chosen, in each case.

EXAMPLE 2

In this Example a test was carried out using concentrate 1 described in Example 1 above. The concentrate fed to the reactor had been milled to give $d_{90} = 10 \mu\text{m}$. The feed slurry concentration was 10 % and the mean residence
5 time of the pulp in the reactor was 2 days. The moderately thermophilic bacterial culture was used at a temperature of 45°C , and the inorganic nutrient solution used was the same as in Example 1. The 25 litre reactor was used in this test.

Following start up, this test was allowed to reach steady operation under conditions where neither dissolved oxygen nor carbon dioxide was limiting
10 the rate of bioleaching. The data for this test over a period of 25 days is shown in Figures 4A-E. The data for days 20 to 28 represent the initial period of steady operation where the redox potential is high (575 – 625 mV). Figures 4B, 4C 4D and 4E show the corresponding data for C_{CO_2} , C_{O_2} , r_{O_2} and copper concentration over the initial high redox potential period. The air flow rate was
15 maintained at 200-230 litres/hour with the inlet air carbon dioxide content fixed at 1800 ppm. During this period the dissolved oxygen was high with concentrations greater than 2 ppm. The dissolved carbon dioxide concentration was also generally high within the range 0.15 to 0.44 ppm.

On day 27 the air flow rate was reduced to 140 litres/hour and
20 further to 90 litres/hour on day 30. The objective here was to manipulate the air flow rate as the basis for controlling the mass transfer supply of carbon dioxide in order to reduce the redox potential to around 430 - 440 mV. It can be seen that C_{CO_2} was maintained at or above its critical value. This ensured that the bacterial cell growth rate was never limited by C_{CO_2} so that the maximum rate
25 of bioleaching was always maintained. This low redox potential range was used since the results of preliminary laboratory testwork had indicated that this provided the optimum conditions for leaching of copper from the chalcopyrite component in this concentrate.

The results in Figures 4A-E show that on day 30 the redox potential had dropped to around 410 mV, which was considered too low and the air flow rate was increased again. By day 33, and up to day 43, the airflow rate could be fixed at a steady value of 170 litres/hour with the redox potential steady in the range 430 – 460 mV. During this period the C_{CO_2} averaged around 0.15 ppm (its critical value), while the C_{O_2} was always 0.3 ppm (above the critical value of 0.2 ppm). Also during this period, it can be seen that the sulphide oxidation rate, as measured by r_{O_2} (Figure 4D), and the concentration of copper leached (Figure 4E) had both increased significantly compared to the initial high redox potential period. This was achieved with C_{CO_2} maintained at or above the critical value.

The data in Figure 4A shows that on day 43 the airflow rate was raised to 185 litre/hour. This proved to be too large an increase. It can be seen that C_{CO_2} increased significantly (well above the critical value; Figure 4B) and consequently the redox potential rose above the set value, r_{O_2} decreased (Figure 4D) and the copper concentration decreased (Figure 4E).

EXAMPLE 3

In this Example a test was also carried out using concentrate 1 described above. The objective of this test was to assess in more detail the optimum redox potential for the bioleaching of this concentrate using the moderately thermophilic bacterial culture.

The 2 litre reactor was used in this test. The concentrate fed to the reactor had been milled to give $d_{90} = 10 \mu m$. The feed slurry concentration was 10 % and the mean residence time of the pulp in the reactor was 1.25 days. The inorganic nutrient solution used was as described in Example 1. The objective of this test was to control the redox potential at different set values by mass transfer control on the carbon dioxide supply, while at the same time maintaining

the maximum rate of bioleaching possible at the specific redox potential. In this test, a platinum and Ag/AgCl reference electrode was immersed permanently in the reactor and connected to a meter and controller. The output from the controller adjusted the impeller stirrer speed to control the mass transfer supply of carbon dioxide thereby maintaining the redox potential at the set point. Where large changes in bioleaching rate were obtained, changes in the airflow rate were also made, but this was done manually. The inlet carbon dioxide content in the air was maintained constant at 2000 ppm.

The results of this test are shown in Figure 5A-C. The redox potential was changed in steps over the range 420 to 520 mV. The data in Figure 5A shows that the rate of bioleaching (oxygen consumption or uptake rate) changed as the redox potential changes within this range. The maximum rate of bioleaching was achieved over the redox potential range 460 to 470 mV, as indicated by the rate of oxygen consumption (Figure 5A) and the concentrations of copper and iron leached (Figure 5C). The oxidation (oxygen consumption) rate observed under these leaching conditions was very high. The C_{CO_2} and C_{O_2} values shown in Figure 5B are daily spot measurements. However, more detailed analyses showed that the values of C_{CO_2} and C_{O_2} exhibited large cyclical (over several hours) changes despite the nominal steady state operating conditions. This was related to the changes in stirrer speed necessary for the controller to maintain the redox potential at the set point coupled with the high air flow rates required to maintain the high oxidation rate attained. The values of C_{CO_2} shown in Figure 5B indicate, however, that C_{CO_2} was always in excess of the critical concentration. The values of C_{O_2} were always maintained well in excess of the critical value.

EXAMPLE 4

In this Example a test was carried out using an extremely thermophilic bacterial culture at 70 °C. The test employed concentrate 2 milled to $d_{90} = 25 \mu\text{m}$. A 25 litre reactor was used with the same nutrient solution as described for Test 1. The mean pulp residence in the reactor was 1.8 days. The feed solids concentration was 5%.

At the start up of this test, the reactor was operated over a sufficient time period (several weeks) so that steady operation was achieved under conditions where the oxygen and carbon dioxide mass transfer was not limiting the rate. Once this had been achieved, the effect of changes in C_{O_2} and C_{CO_2} on the oxidation and growth rates was investigated. In the case of C_{O_2} , this was accomplished solely by changes in the airflow rate to the reactor, keeping the stirrer speed and the inlet air carbon dioxide content constant. In the case of C_{CO_2} this was accomplished by a combination of changes in the airflow rate to the reactor and the inlet air carbon dioxide concentration, again with the stirrer speed kept constant. The approach taken was to carry out these changes over short periods of time (non-steady state approach). However, the time periods were kept sufficiently short (less than one hour) so that the changes in the steady state cell concentrations were effectively negligible.

The results of these tests are shown in Figures 6 and 7 for oxygen and carbon dioxide, respectively. Figure 6 indicates that the critical value of C_{O_2} for the extremely thermophilic culture used is in the range 0.5 – 0.7 ppm. Figure 7 indicates that the critical value of C_{CO_2} for the extremely thermophilic culture is in the range 0.6 – 0.7 ppm.

Following the above tests, the reactor was then run under conditions where the carbon dioxide and oxygen supply were again sufficient to maintain C_{CO_2} and C_{O_2} well in excess of their respective critical values. Under these conditions a

high redox potential was maintained in the process. Following this initial phase, the reactor was then run under conditions where the carbon dioxide supply was mass transfer limited in order to control and maintain the redox potential at a low value. A summary of the results obtained is given in Table 1. The objective of these tests was to assess the effect of these operating conditions on the levels of oxidation of the chalcopyrite and pyrite components in the concentrate.

During the initial "unlimited" phase, the conditions used allowed both C_{CO_2} and C_{O_2} to be maintained in excess of their critical values. The data in Table 1 shows that this was achieved and the redox potential was high (578 mV). Under these conditions, high levels of oxidation for both chalcopyrite and pyrite were obtained (76 and 83 %, respectively). During the second carbon dioxide-mass transfer-limited phase, C_{CO_2} was maintained at or near to the critical value (0.6 – 0.7 ppm) and the redox potential was maintained at 437 mV. It was observed that at the lower redox potential there was a minor increase in the level of chalcopyrite leached compared to that observed at the high redox potential. If the lower redox potential has an enhancing effect on chalcopyrite bioleaching at 70 °C, it does not seem be as pronounced as that observed at the lower temperature. The major effect of the lower redox potential is on the bioleaching of pyrite. The pyrite leached at 437 mV was only 35% compared to 83% at 578 mV. For a process treating the present concentrate (concentrate 2), the ability to control the redox potential, and hence the amount of pyrite oxidised, could provide a major process advantage. For the complete oxidation of all the chalcopyrite and pyrite sulphide, the process would produce excess acid that would need to be neutralised with a neutralising agent such as limestone. This would be a very significant addition to the operating costs of the process. The added costs of power to promote the mass transfer supply of the oxygen required for pyrite oxidation and for the corresponding additional cooling load, can be avoided by employing the method of the invention.

TABLE 1

	EXCESS CO ₂ SUPPLY	MASS TRANSFER- LIMITED CO ₂ SUPPLY
Redox potential (mV, Ag/AgCl)	578	437
pH	1.55	1.77
C _{O2} (ppm)	2.11	1.8
C _{CO2} (ppm)	0.9	0.6 - 0.7
Sulphide leached:		
Chalcopyrite (%)	76	84
Pyrite (%)	83	35

The Examples described above show how the gas-mass transfer control of carbon dioxide advantageously can be used to maintain the dissolved carbon dioxide concentration at or above a critical lower limit as a means of controlling the slurry redox potential at a chosen value. Advantageously, this can be done while simultaneously maintaining the rate of bioleaching at its maximum. Thus, the method of the invention allows effective manipulation of a bioleaching process to achieve a desired level of redox potential.

In the case of chalcopyrite leaching, the method of the invention provides a mass transfer control strategy that maintains the dissolved carbon dioxide concentration at all times at or above its critical lower limit, thereby reducing the redox potential from its normally high level (600 mV) to a low level (430 mV), advantageously achieving stable operation. It is also to be appreciated that, since the leaching rate of chalcopyrite improved significantly at lower redox potential levels, the final control level for mass transfer supply of carbon dioxide

that needed to be sustained is significantly higher than that required at the high redox potential levels.

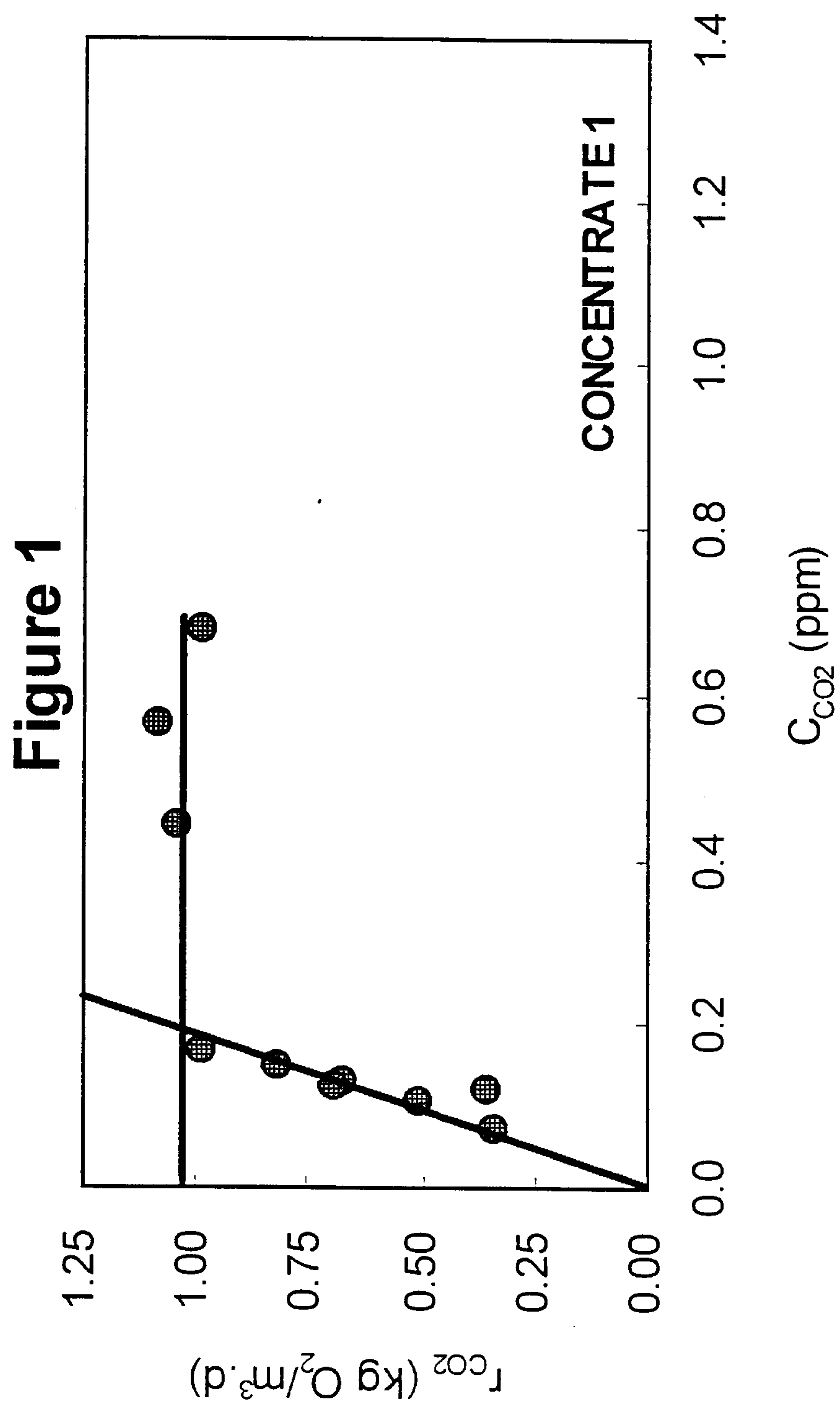
Copper sulphide concentrates often contain significant quantities of pyrite (FeS_2). At high redox potentials (> 500 mV) the pyrite component will leach rapidly and will significantly contribute to the overall level of oxidation (ferric iron consumption) observed. Under low redox potential conditions (< 450 mV) the level of pyrite oxidation becomes negligible. Control of redox potential therefore provides an effective method for controlling the oxidation of this sulphide. The pyrite component is not usually a valuable component of copper concentrates and the advantage accruing in preventing pyrite oxidation would be a reduction in the process power costs for air supply and cooling. Also, if the pyrite is allowed to leach the process may produce excess acid and there would be an added cost penalty to neutralise and dispose of this acid. On the other hand, other copper concentrates may be acid deficient and the ability to control the leaching of pyrite to produce "just enough" acid advantageously results in an economic benefit.

CLAIMS:

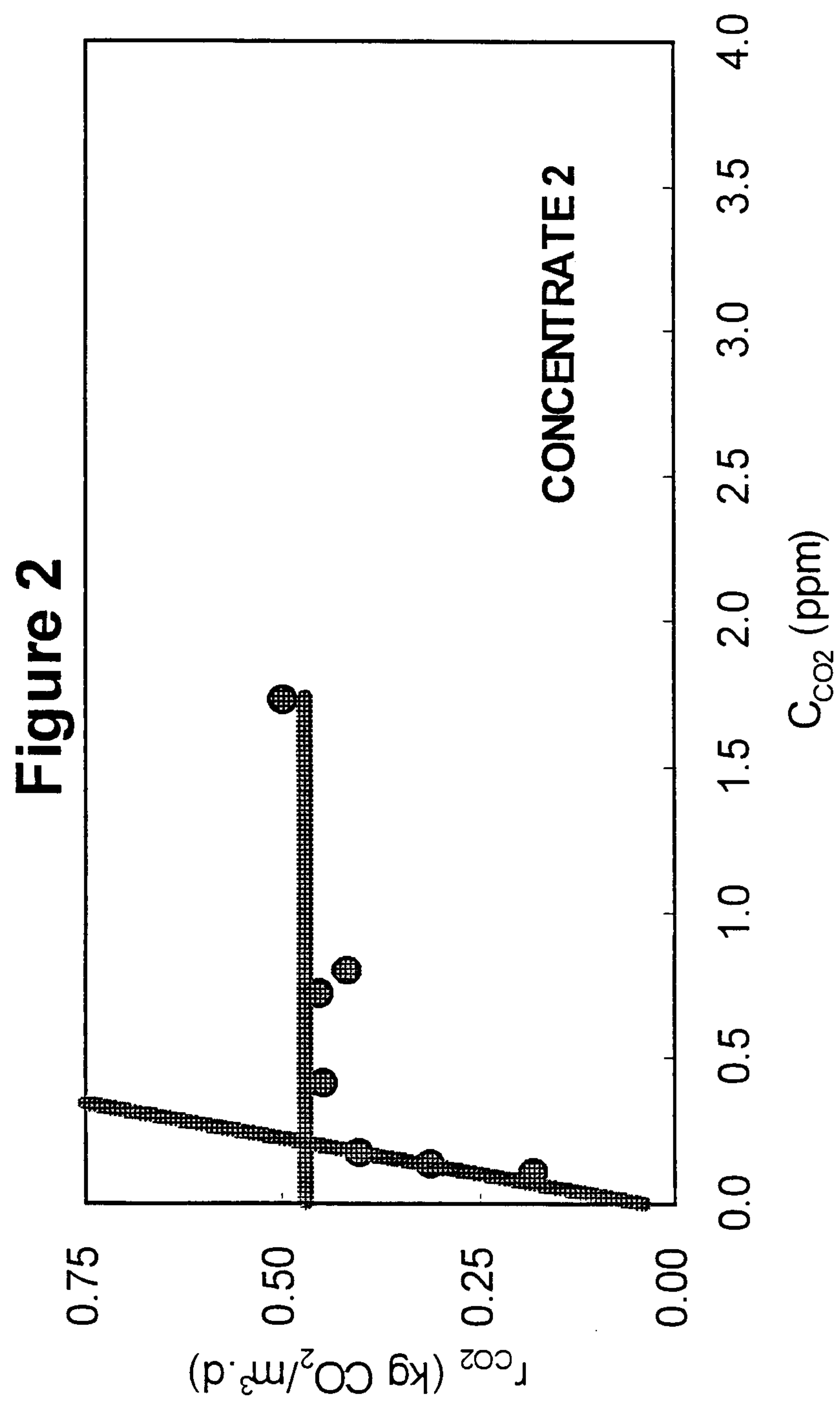
1. A method of operating a bioleach process for the leaching of a sulfide bearing ore or concentrate, the method including
subjecting a bioleach slurry which includes dissolved oxygen, dissolved carbon dioxide, sulphide and microorganisms to a bioleach stage; and
controlling the redox potential of the bioleach slurry within a predetermined range, by controlling the concentration of at least one of the dissolved oxygen and the dissolved carbon dioxide in the bioleach slurry, while ensuring that both the dissolved oxygen concentration and the dissolved carbon dioxide concentration in the bioleach slurry remains above respective lower concentration limits,
the respective lower concentration limits being selected to ensure that the growth of the microorganisms is not limited by a too low concentration of either the dissolved oxygen or the dissolved carbon dioxide in the bioleach slurry,
the redox potential being controlled in the range of 380 mV to 450 mV relative to an Ag/AgCl reference electrode when the ore or ore concentrate includes pyrite as an undesirable component thereby inhibiting leaching of the pyrite while selectively leaching desirable sulphide minerals present in the ore or ore concentrate with a rest potential which is lower than the rest potential of pyrite,
and in the range of 380 mV to 480 mV relative to an Ag/AgCl reference electrode when the ore or ore concentrate includes chalcopyrite as a predominant sulphide component, thereby to promote the rate and extent of chalcopyrite oxidation.
2. A method as claimed in claim 1, in which the microorganisms comprise a moderately thermophilic bacterial culture and the lower concentration limit for both the dissolved carbon dioxide and the dissolved oxygen in the bioleach slurry is 0.2 ppm.

3. A method as claimed in claim 2, in which the microorganisms comprise an extremely thermophilic bacterial culture, the lower concentration limit for dissolved carbon dioxide in the bioleach slurry being 0.6 ppm and the lower concentration limit for dissolved oxygen in the bioleach slurry being 0.5 ppm.
4. A method as claimed in any one of claims 1 to 3, in which the redox potential of the bioleach slurry is controlled within the predetermined range by controlling the concentration of the dissolved carbon dioxide in the bioleach slurry.
5. A method as claimed in any one claims 1 to 4, which includes supplying carbon dioxide and oxygen to the bioleach slurry in the form of carbon dioxide-enriched air.
6. A method as claimed in any one of claim 1 to 4 inclusive, in which the bioleach slurry is acidic and which includes supplying carbon dioxide to the bioleach slurry in the form of limestone.
7. A method as claimed in any one of claims 1 to 4 inclusive, in which the bioleach slurry includes microorganisms with enzymes in their cells which are capable of reacting with urea to release carbon dioxide, the method including supplying carbon dioxide to the bioleach slurry in the form of urea.

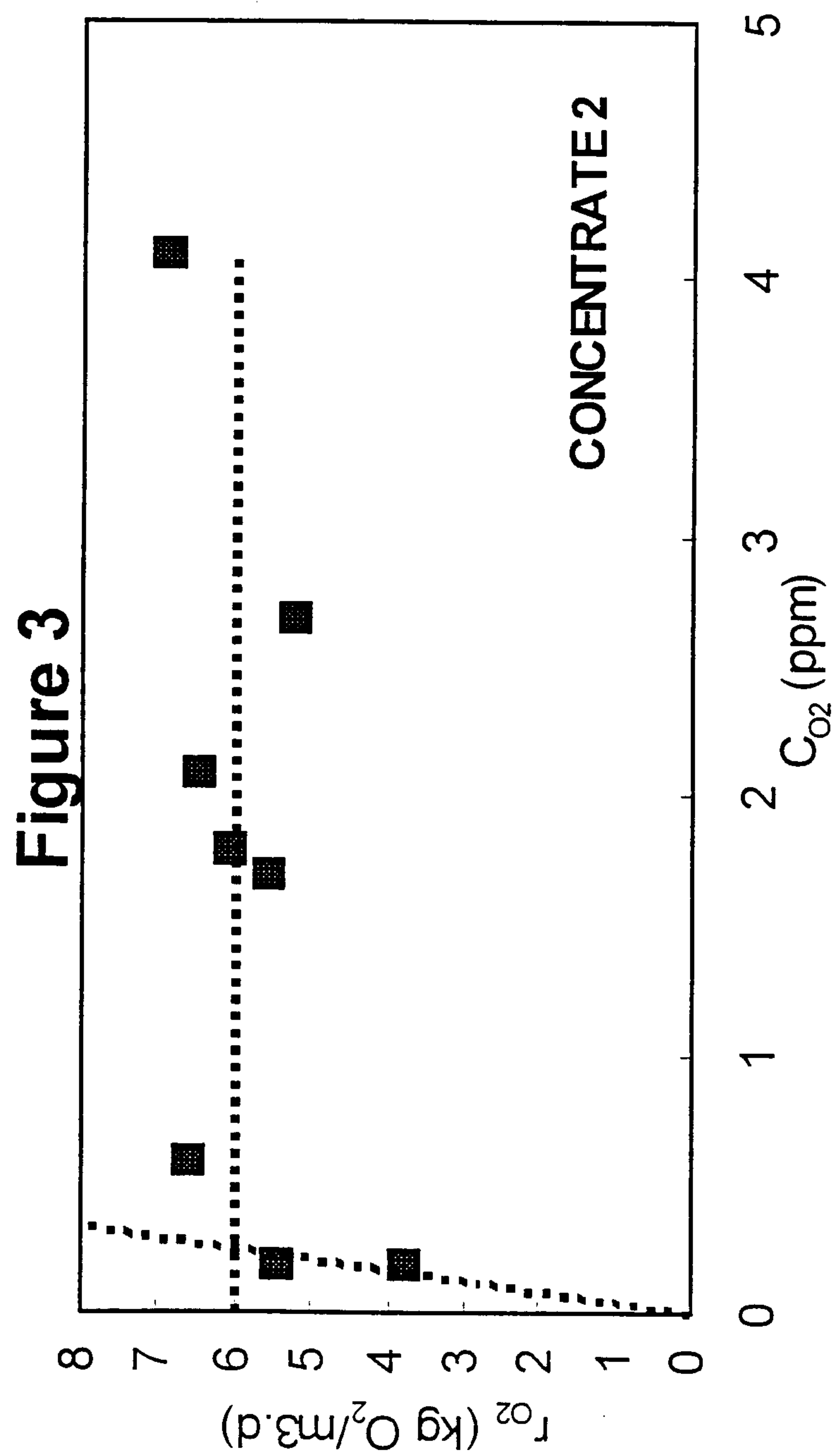
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FIGURE 4a

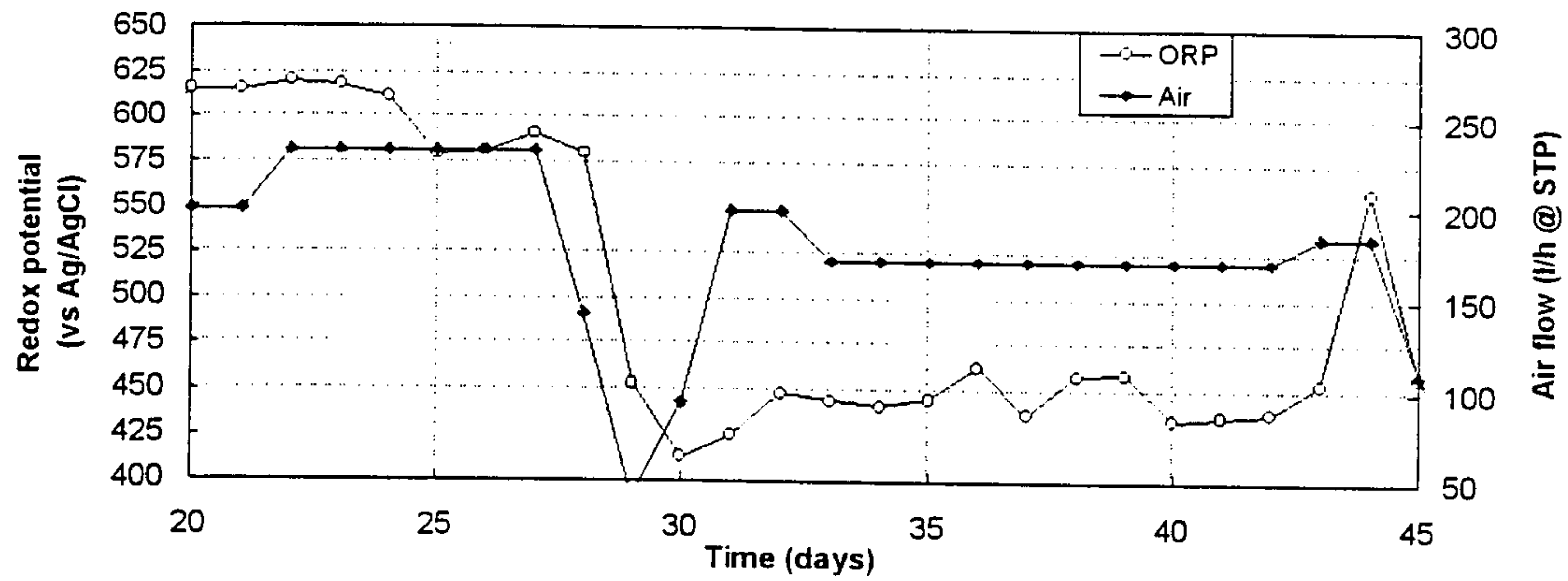


FIGURE 4b

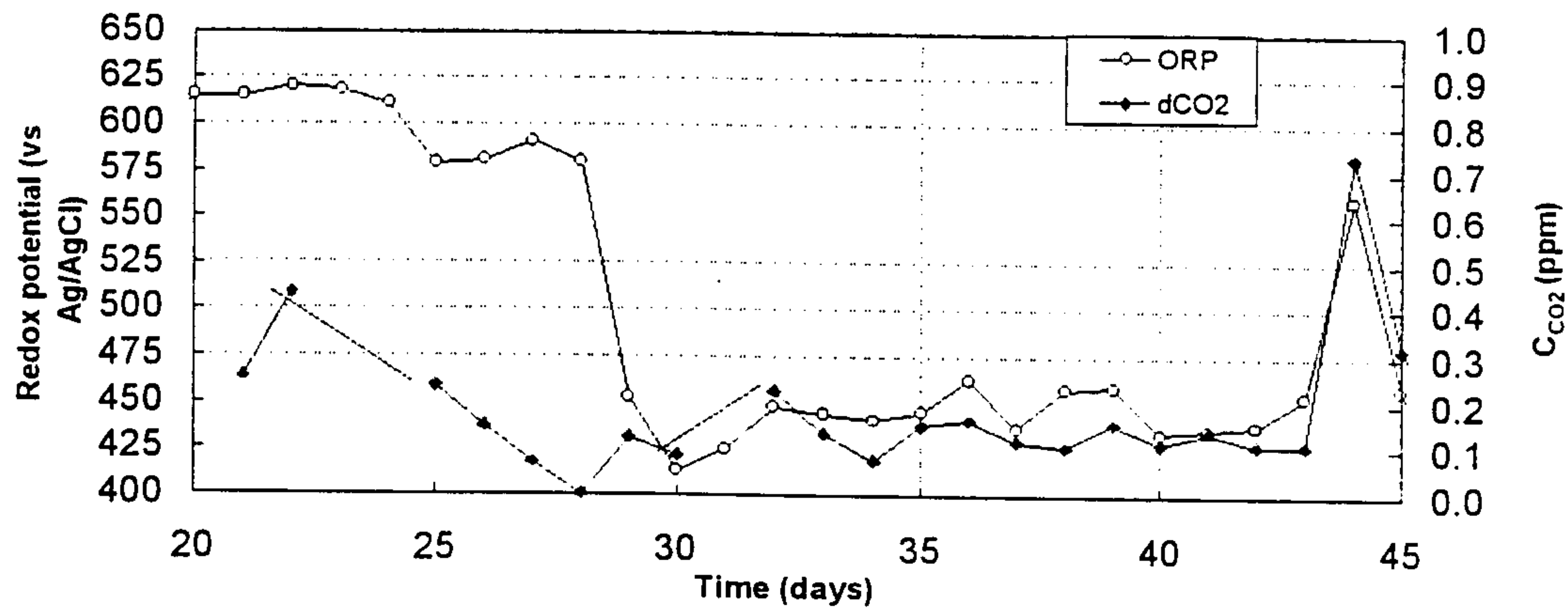
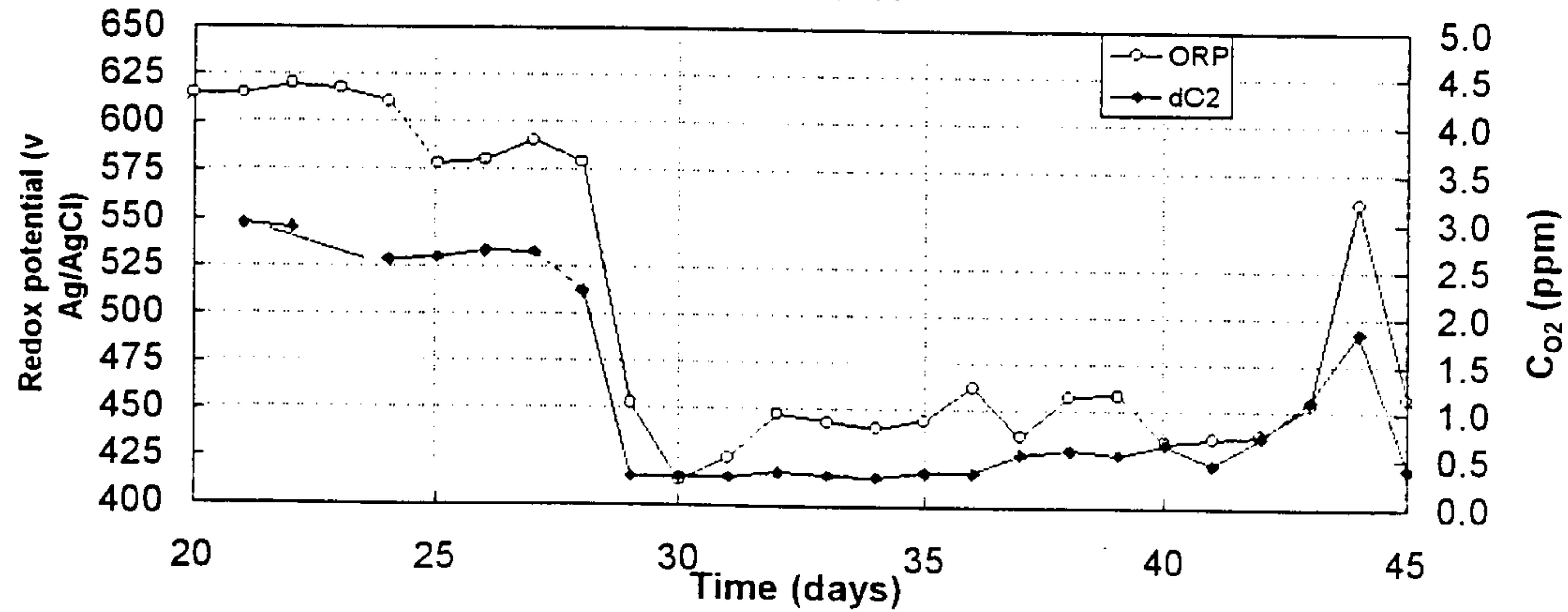


FIGURE 4c



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FIGURE 4d

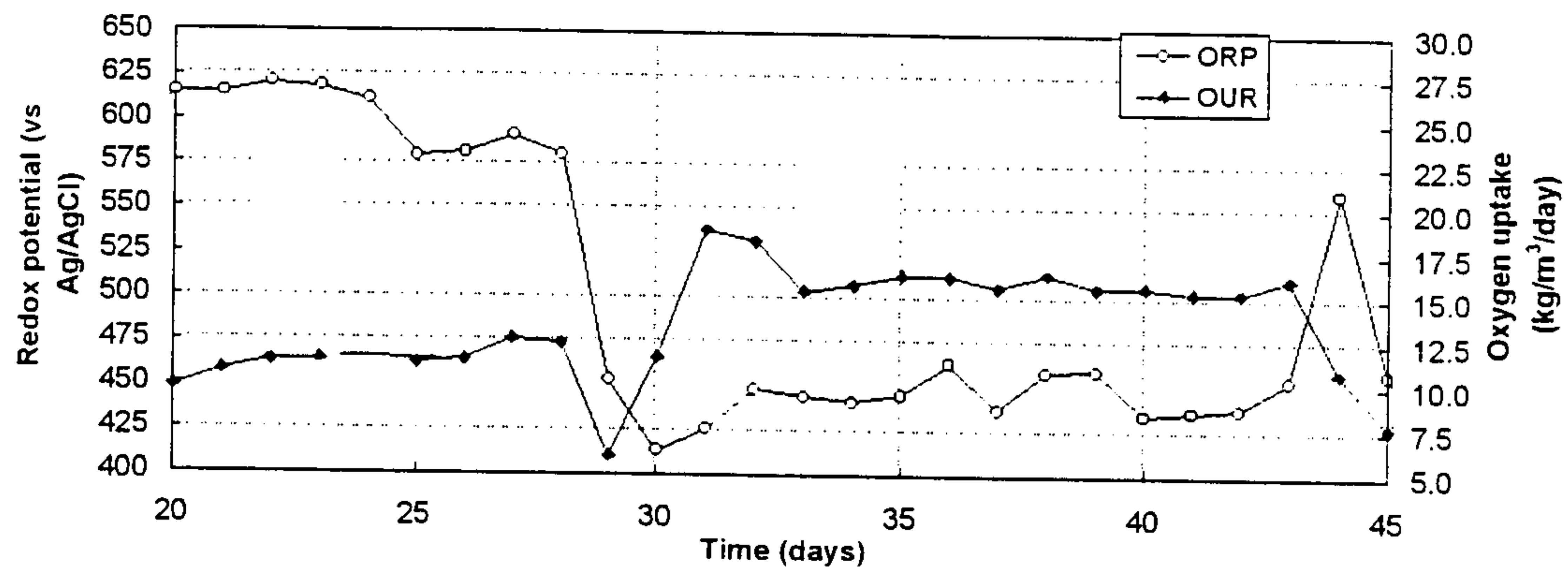
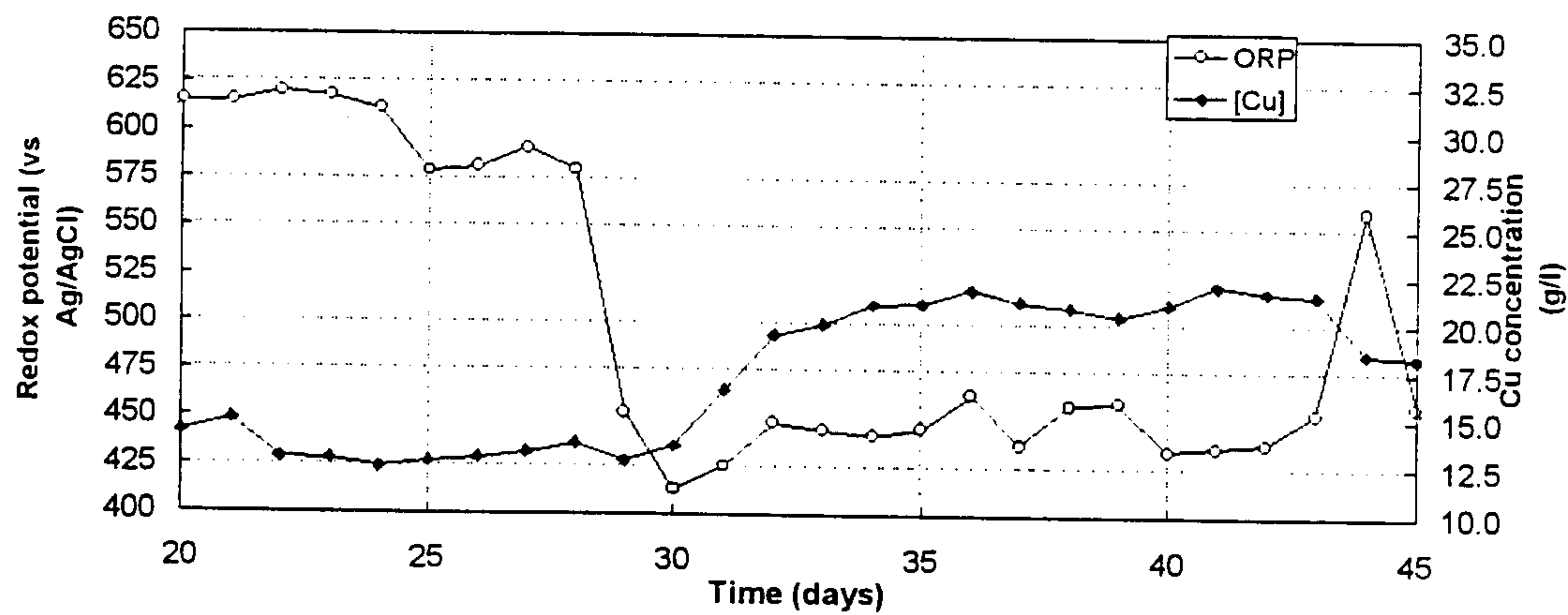


FIGURE 4e



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Figure 5A

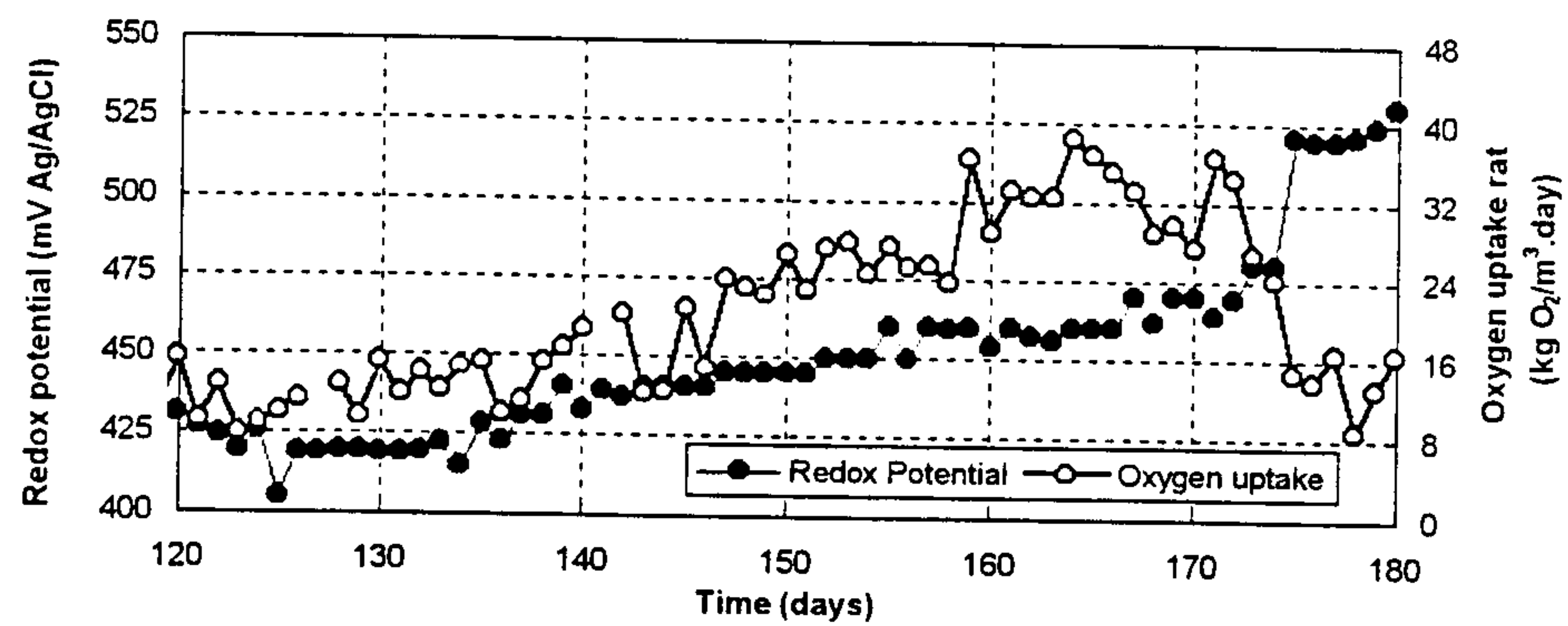


Figure 5B

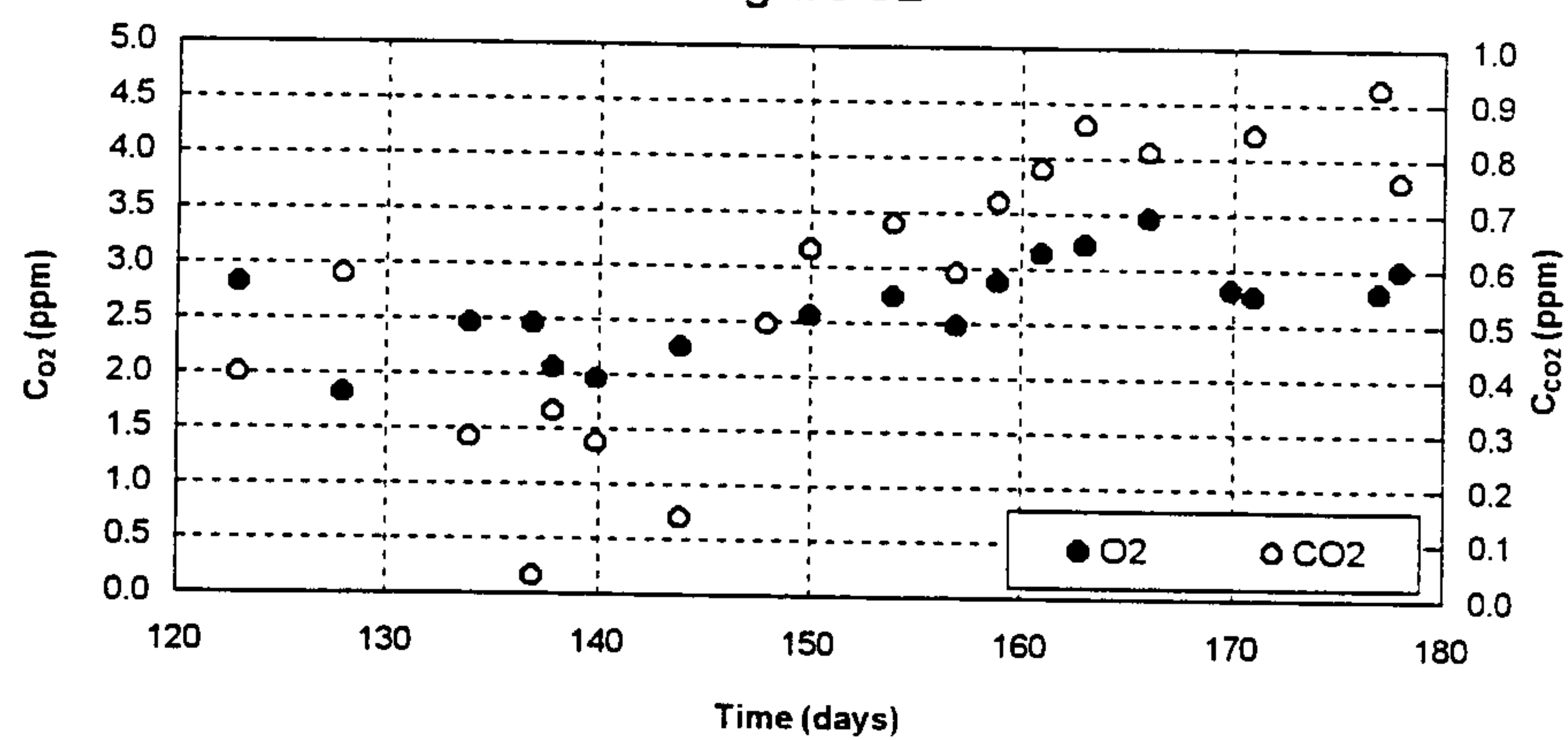
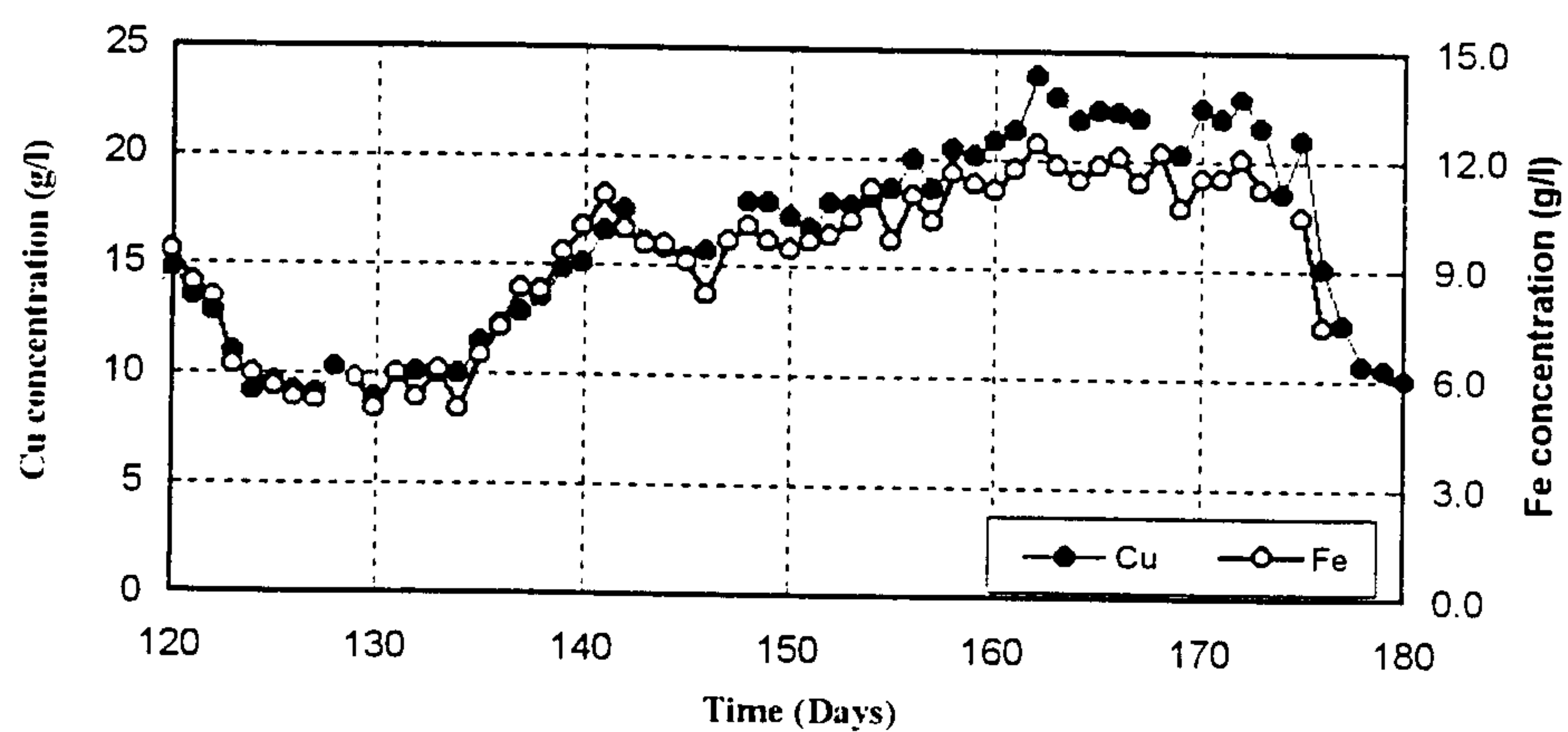
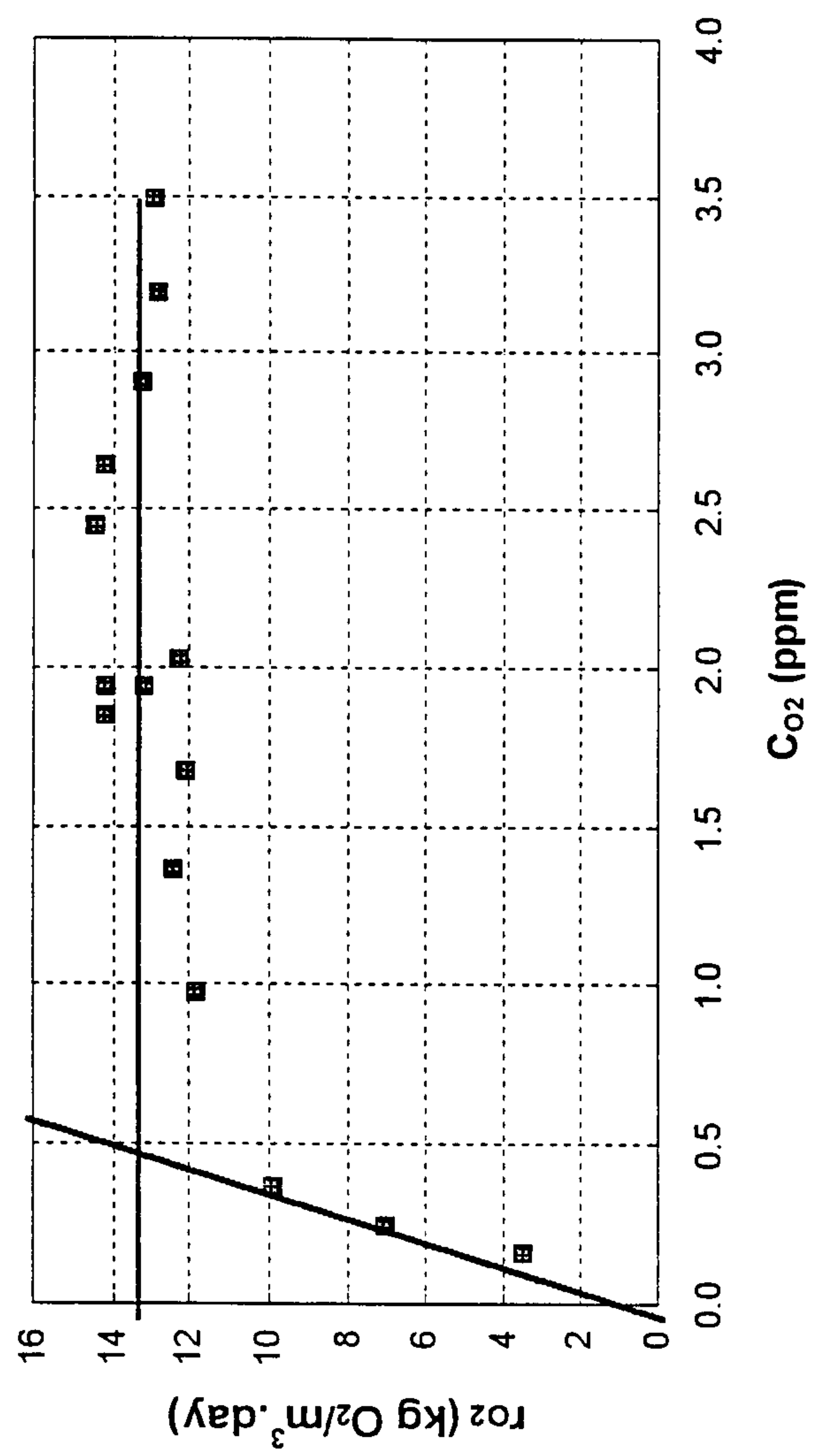


Figure 5C



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Figure 6



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